

Valid internal standard technique for arson detection based on gas chromatography–mass spectrometry

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ABSTRACT

The most popular procedures for the detection of residues of accelerants in fire debris are the ones published by the American Society for Testing and Materials (ASTM E1412-07 and E1618-10). The most critical stages of these tests are the conservation of fire debris from the sampling to the laboratory, the extraction of residues of accelerants from the debris to the activated charcoal strips (ACS) and from those to the final solvent, as well as the analysis of sample extract by gas chromatography–mass spectrometry (GC–MS) and the interpretation of the instrumental signal. This work proposes a strategy for checking the quality of the sample conservation, the accelerant residues transference to final solvent and GC–MS analysis, using internal standard additions. It is used internal standards ranging from a highly volatile compound for checking debris conservation to low volatile compound for checking GC–MS repeatability. The developed quality control (QC) parameters are not affected by GC–MS sensitivity variation and, specifically, the GC–MS performance control is not affected by ACS adsorption saturation that may mask test performance deviations. The proposed QC procedure proved to be adequate to check GC–MS repeatability, ACS extraction and sample conservation since: (1) standard additions are affected by negligible uncertainty and (2) observed dispersion of QC parameters are fit for its intended use.

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1. Introduction

Arson is a crime difficult to investigate since evidences at the crime scene are frequently destroyed by fire. The cause of fire is investigated through the interpretation of the fire scenario and by the collection of chemical evidences of the presence of fire accelerants residues. Whenever accelerants finger-prints are observed in the deflagration point, it must be investigated possible criminal origin of fire.

Since accelerant residue detection affects decisively the course of fire investigation and constitutes major material evidences of the crime, the reliability of these tests are of utmost importance.

The most widely used standards for the detection of ignitable liquid residues (ILRs) in fire scenarios are the ones issued by the ASTM. These standards are divided into the involved pre-analytical and analytical steps. ASTM standards E 2451-08 [1], E 1412-07 [2] and E 1618-10 [3] describing sample preservation from sampling to laboratory, sample extraction and, GC–MS extract analysis

respectively, are within the most used standards. The ASTM E 1412-07 standard [2] describes a passive headspace concentration of volatile sample components in ACS followed by solvent extraction of ILR from ACS. The ASTM E 1618-10 standard [3] describes both GC–MS signals production and interpretation.

The ASTM E 1412-07 standard [2] suggests the addition of an internal standard to the sample to allow the ILR extraction control. Nevertheless, no standard addition procedure is proposed in this standard. Several authors [4–8] highlighted the merits of using internal standard techniques in arson detection but there were no detailed control procedures or performance data shown.

The stage where internal standard is added defines the controlled pre-analytical and/or analytical stages. The addition of internal standard, controls the combined performance of subsequent stages. A sequence of additions of several internal standards in different stages allows the identification of the cause of observed deviation by identifying the stage where deviation is observed first. This information is useful to decide adequate corrective measures that may vary from GC–MS analysis repetition to collected sample rejection due to its inadequate conservation. This control is particularly important to avoid false native results (e.g. the wrong conclusion about the absence of ILRs in fire debris).

The selected internal standard compound and the way it is introduced in the pre-analytical or analytical stage affects the adequacy of the control procedure. Thermolabile compounds are inadequate

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to be used as internal standards to GC analysis since the variability of their chromatography masks performance deviation. The internal standard addition must not be highly uncertain, for instance by the inadequate use of volumetric material, since it will affect the validity (e.g. adequacy for the intended use) of the quality control procedure.

Since GC-MS sensitivity can vary from one day to another, due to variations in uncontrolled experimental conditions, the assessment of the performance of the procedure must be able to compensate this effect. The performance of analytical steps controlled by the addition of internal standard after ACS sample extraction may be masked by the variability of internal standard adsorption to ACS saturated with sample compounds. The outcome of the competition between the adsorbed sample components and the internal standard is known to be extremely variable. This phenomenon can be overcome by adding internal standard after the removal of ACS from the extract.

This work presents a valid and user-friendly procedure for the control of most critical stages of arson detection individually, namely (1) sample conservation from sampling to laboratory; (2) sample components extraction and (3) GC-MS analysis. The validity of the procedure is supported by the ability to detect deviations of the performance not masked by standard addition uncertainty, by GC-MS sensitivity variations or by sample dependent effects. The test quality control is based on checking the value of defined parameters considering statistically and metrologically sound criteria.

2. Experimental

2.1. Reagents and standards

Chemicals of GC-grade purchased from Merck were used.

The following standards were used (CAS number/producer/purity): 1,4-dichlorobenzene, DCB (CAS 106-46-7/Alfa Aesar/99%), cyclohexylbenzene, CHB (CAS 827-52-1/Alfa Aesar/98%) and tetrachloro-m-xylene, TCMX (CAS 877-09-8/Supelco Analytical/97.5%). Individual standard solutions of DCB (S_{DCB}), CHB (S_{CHB}) and TCMX (S_{TCMX}), with mass fractions of 3.77×10^{-3} for DCB (w_{DCB}) and 3.77×10^{-4} (w_{CHB} and w_{TCMX}) for CHB and TCMX, were prepared by diluting 250 mg or 25 mg of pure substance in 66.322 g of dichloromethane (DCM).

Activated charcoal strips (ACS) (9 mm × 20 mm each) were purchased from Albrayco Technologies, Inc. (Cromwell, CT).

A mixture of DCM and pentane (P) with a mass fraction, w_{DCM-P} , of DCM of 0.679 (mixture of similar volumes of both solvents), solution A, was prepared to extract adsorbed compounds from ACS.

A standard solution, S_{Ref} , with a concentration, C_{Ref} , of 93.9 mg L^{-1} of TCMX was prepared by diluting m_A mass of S_{TCMX} (measured with pipette P1 adjusted for 200 μL) through addition of m_B mass of solution A (measured with pipette P1 adjusted for 800 μL). C_{Ref} was estimated from w_{TCMX} , m_A , m_B and a model of the variation of solution density with DCM mass fraction (Section 2.6.1).

2.2. Equipment

The following equipment was used:

The analytical balance Mettler AE100 was purchased from Mettler-Toledo International (Greifensee, Zürich, Switzerland);

The oven Heraeus model KT500 was purchased from Thermo-Scientific (Waltham, MA, USA);

The micropipette (P1) VWR volume 100–1000 μL was purchased from VWR International, LLC (Radnor, PA, USA);

Table 1
Sample codification and description.

Code	Accelerant	Burned fraction (%)	Delay between the burning and the analysis (h)
ACPU1	Gasoline 95	75	24
ACPU2	Gasoline 95	50	24
ACPU3	Gasoline 95	25	24
ACPU4	Gasoline 95	100	0
ACPU5	Gasoline 98	75	24
ACPU6	Gasoline 98	75	72
ACPU7	Gasoline 98	50	24
ACPU8	Gasoline 98	50	72
ACPU9	Gasoline 98	25	24
ACPU10	Paint thinner	100	0
ACPU11	Solid charcoal starter	100	0
ACPU12	White spirit	100	0

The dispenser (D1) BrandTech, model Dispensette III Bottletop Dispenser 0.5–5 mL was purchased from BrandTech Scientific, Inc. (Essex, CT, USA);

Details of GC-MS equipment are provided in Section 2.5.

2.3. Samples

Five types of accelerants, often detected in arson scenes, were studied, namely: 95 octane gasoline, 98 octane gasoline, paint thinner, solid charcoal starter and white spirits. These accelerants were purchased from a local petrol station and drugstore.

Defined portions of the different accelerants were burned and recovered in a glass jar, equivalent to the ones used to collect real samples, to different extensions producing 12 simulated fire debris samples. The internal standard for sample conservation control was added to glass jar after fire extinction and cooling to room temperature. The jar was capped after internal standard addition. Different delays between combustion and ILR extraction were considered to simulate different delays between sample collection and laboratory analysis. Table 1 details the burning test conditions and the delay from first internal standard addition and ILR detection. The burned portion of liquid accelerants was 5 mL. A mass of 4.5 g of solid charcoal starter, the only solid accelerant, was burned in glass jar coded "ACPU11".

2.4. Procedure

Fig. 1 describes the pre-analytical and analytical procedure.

For each sample, a mass m_1 of solution S_{DCB} , measured with pipette P1 adjusted to 500 μL , is added before jar capping. Since the used volumetric material is calibrated for measuring water volumes, the delivered solutions were measured gravimetrically as its performance may vary significantly for organic solvents. The mass of delivered solution estimated in an occasion is considered in subsequent routine tests and verified every six months to detect equipment malfunction.

At the laboratory and immediately before analysis, the glass jar is uncapped, mass m_2 of solution S_{CHB} (measured with pipette P1 adjusted to 500 μL) added to debris, ACS is positioned in the head space of the glass jar using an inert support and the capped jar is warmed up to $80 \pm 1^\circ\text{C}$ for 14.0 ± 0.5 h in the oven. Subsequently, the glass jar is cooled at room temperature for about 4 h, the ACS is transferred from the glass jar to vial 1 (2.0 mL) and immersed in a mass, m_3 , of solution A (added through dispenser D1 adjusted to 1 mL). The immersed ACS is subjected to occasional hand mixing for 30 ± 5 min. The ACS extract is transferred to another previously weighed vial 2 (2.0 mL) (m_4 -mass of the vial and cap) and the mass

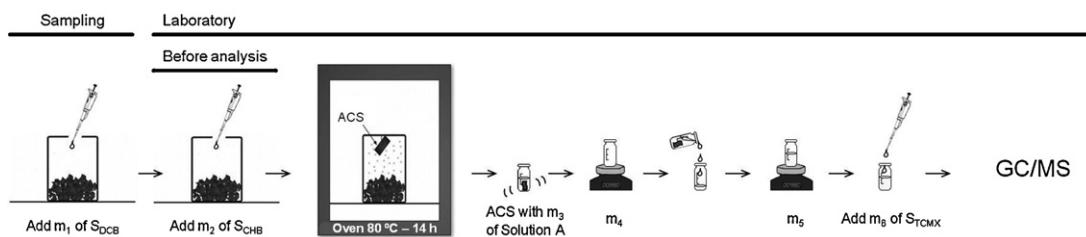


Fig. 1. Scheme of the analytical procedure, where: m_1 : mass of individual standard solution of 1,4-dichlorobenzene added; m_2 : mass of individual standard solution of cyclohexylbenzene added; m_3 : mass of solution A (mixture of dichloromethane and pentane) added to activated charcoal strip for the extraction of ILR; m_4 : mass of the empty vial + cap; m_5 : mass of the vial + cap + activated charcoal strip extract; m_6 : mass of individual standard solutions of tetrachloro-m-xylene added to activated charcoal strip extract in the vial.

of the vial + cap + solvent, m_5 , measured. A mass m_6 of S_{TCMX} solution is added to extract in the vial, using pipette P1 adjusted to 200 μ L, and the mixed solution analysed by GC-MS (Section 2.5). The heights of the peaks of molecular ion of DCB (m/z 146 amu), CHB (m/z 160 amu), and TCMX (m/z 244 amu), respectively H_{DCB} , H_{CHB} , and H_{TCMX} , of the sample are recorded.

The standard solution, S_{Ref} (external standard) is injected before and after samples to check instrumental sensitivity. The heights of the peaks of the molecular ion of TCMX, H_{Ref} , of this reference are recorded. Both signals from standard ($H_{Ref(1)}$ and $H_{Ref(2)}$ for the first and the second injection, respectively) are compared considering the repeatability (s_r) of analysis using the repeatability limit (r) concept [9]. The following quality control criterion was used: $|H_{Ref(1)} - H_{Ref(2)}| \leq r = 2.8s_r$.

One blank sample is analysed in each samples batch. The blank sample is prepared by adding the first and the second internal standards, S_{DCB} and S_{CHB} , respectively, to an empty jar. Then the blank sample is subjected to the same analytical procedures as the samples. Deviations in internal standard results or observed relevant contaminants must be solved to protect sample assays.

The identification of ILR in fire debris is based on total ion count GC-MS chromatograms [2], while internal standards are checked through the molecular ion signal to protect tests quality control from sample interference. The studied internal standards are unlikely to be detected in fire debris [4–8] and present an equivalent volatility to ILR, that guarantees a direct correlation between the observed deviations in internal standard and ILR signals.

2.5. GC-MS conditions

The extracts are analysed on an Agilent GC-MS 6890-5973N (Agilent Technologies, Palo Alto, CA, USA) equipped with a fused silica chromatography column (30 m \times 0.25 mm ID and 0.25 μ m film thickness) of crosslinked 100% polydimethylsiloxane (HP-1). The carrier gas is helium (purity 99.9995%) at a flow rate of 1.2 mL min $^{-1}$. Injections (1 μ L) are performed with an autosampler Agilent 7683 Series in split mode (1:20) to an inlet temperature of 300 °C. The oven temperature programme used is: initial temperature at 60 °C for 6 min, then at 20 °C min $^{-1}$ rising to 280 °C and hold for 8 min, increasing 10 °C min $^{-1}$ up to 300 °C and kept constant for 3 min. The total run time is 29 min (Fig. 2). The quadrupole MS is operated in positive full scan mode for a mass range of m/z 20–400 amu. The conditions of the ion source are: energy of the electrons 70 eV and current emission of 34.6 μ A. The mass spectra are obtained and processed using the Chemstation G1701 CA version C.00.0021.

2.6. Internal standard technique

The following sections describe the validation and quality control of GC-MS analysis repeatability (Section 2.6.1), accelerant

residues extraction (Section 2.6.2) and sample conservation (Section 2.6.3).

2.6.1. GC-MS repeatability

2.6.1.1. TCMX concentration. The concentration of TCMX in the sample extract (C_{TCMX} ; mg L $^{-1}$) is estimated from the mass of TCMX, m_{TCMX} ($m_{TCMX} = m_6 w_{TCMX}$) and total volume (V_E) of the extract ($C_{TCMX} = m_{TCMX} / V_E$). The volume V_E is estimated from the mass fraction of DCM in the extract, w_{DCM} (Eq. (1)), total mass of solution m_E ($m_E = m_5 - m_4 + m_6$) and a model of the variation of solution volumetric mass, ρ , with w_{DCM} (ρ vs. w_{DCM}).

$$w_{DCM} = \frac{(m_5 - m_4) \cdot w_{DCM-P} + m_6(1 - w_{DCM})}{m_5 - m_4 + m_6} \approx \frac{(m_5 - m_4) \cdot w_{DCM-P} + m_6}{m_E} \quad (1)$$

The V_E is estimated from the volumetric mass of the extract, ρ_E , interpolated from the model (ρ vs. w_{DCM}): $V_E = m_E / \rho_E$.

The variation of the volumetric mass, ρ , between 0.648 and 0.800 w_{DCM} values is adequately described by the linear unweighted regression model ($\rho = a + b \cdot w_{DCM}$; where a is the intercept and b the slope of the regression line). The regression parameters are calculated from the following equations:

$$b = \frac{\sum_i^n (x_i - \bar{x})(y_i - \bar{y})}{\sum_i^n (x_i - \bar{x})^2} \quad (2)$$

$$a = \bar{y} - b\bar{x} \quad (3)$$

where x_i and y_i are the w_{DCM} and ρ values of each one of the n points of the graph ρ vs. w_{DCM} , and \bar{x} and \bar{y} are the average of all n values of x_i and y_i , respectively [10].

2.6.1.2. Quality control procedure. The GC-MS repeatability is checked by comparing the heights of TCMX molecular ion peaks of the first analysis of S_{Ref} solution, H_{Ref} , and sample extract, H_{TCMX} , taking in account the fact that C_{TCMX} may be significantly different from C_{Ref} (≈ 94 mg L $^{-1}$ of TCMX). The factor γ_{TCMX} is calculated from Eq. (4):

$$\gamma_{TCMX} = \frac{H_{Ref}}{(H_{TCMX} \cdot C_{Ref} / C_{TCMX})} \quad (4)$$

where the denominator of Eq. (4) is the predicted height of TCMX molecular ion peak for a solution with C_{Ref} concentration using sample extract signal, H_{TCMX} , as reference.

The γ_{TCMX} value is affected twice, for H_{Ref} and H_{TCMX} , by GC-MS injection and detector signal repeatability, and by the reliability of estimated C_{Ref} and C_{TCMX} values. In case where no significant deviations affect estimated C_{Ref} and C_{TCMX} values occur, the γ_{TCMX} parameter is expected to be equivalent to one with random variations above and below this value.

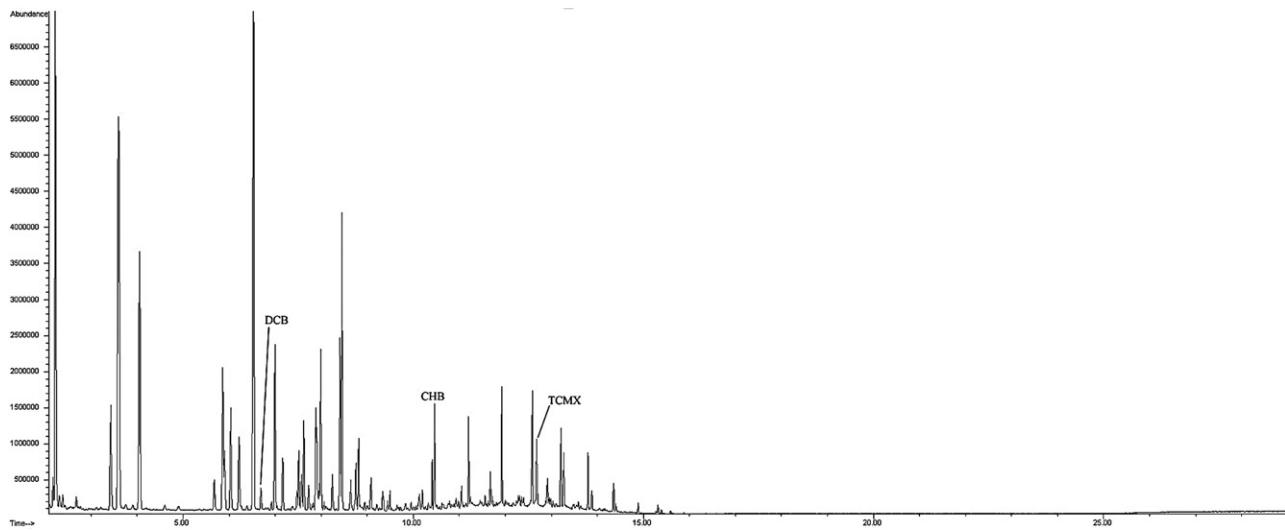


Fig. 2. Total ion current from sample ACPU1 extract.

2.6.1.3. Validation. The validation of the GC–MS repeatability control involved two evaluations, namely: (1) the comparison of the relative standard uncertainty, u'_R , associated with the ratio R ($R = C_{\text{Ref}}/C_{\text{TCMX}}$) with the coefficient of variation, CV_{R_H} , of the ratio R_H ($R_H = H_{\text{Ref}}/H_{\text{TCMX}}$) and (2) the evaluation of the experimental variation of γ_{TCMX} values. The u'_R must be negligible considering CV_{R_H} . The CV_{R_H} is $\sqrt{2}$ larger than the coefficient of variation, CV_{Rep} , of peak heights ($CV_{R_H} = \sqrt{2} \cdot CV_{\text{Rep}}$) [9]. The CV_{Rep} was estimated from heights of TCMX molecular ion peaks of duplicate analysis of different samples extracts. These duplicates were obtained in repeatability conditions (e.g. same operator, equipment and in a short period of time). The CV_{Rep} was calculated from the standard deviation of n ($i = 1$ to n) relative differences of duplicates results (d'_i) [$d'_i = (d_{1i} - d_{2i})/\bar{d}_i$; where d_{1i} , d_{2i} and \bar{d}_i are duplicate results and their average, respectively].

The experimental variation of γ_{TCMX} values is assessed from replicated measurements performed in samples from different matrices (Section 2.2).

Evaluation of the uncertainty associated with R . The uncertainty associated with R is estimated from the algebraic relation used to calculate this parameter and the standard uncertainty associated with the input quantities. The equation used to calculate R will allow to cancel the effect of some uncertainty components, like the ones related with the preparation of S_{TCMX} solution since this solution is used to prepare samples and external standards. The standard uncertainties of the input quantities were combined using the numerical Kragten method [11,12]. The u'_R should be approximately five times smaller than CV_{R_H} to be negligible and consequently adequate for this control.

Evaluation of the variation of γ values. The variability of γ_{TCMX} values is quantified by the coefficient of variance ($CV_{\gamma_{\text{TCMX}}}$) of a set of γ_{TCMX} values obtained from tests performed on different days and types of samples. The $CV_{\gamma_{\text{TCMX}}}$ must be small enough to allow to identify deviations in GC–MS repeatability that can affect ILR detection. No adequate references are known by the authors to define the target value for this CV.

2.6.1.4. Quality control criterion. The routine control of GC–MS repeatability is performed by the calculation of a γ_{TCMX} value for each sample analysis and the evaluation of its positioning within the interval from Eq. (5). If this criterion is not fulfilled

and no ILRs are detected in sample, sample extract must be reinjected.

$$\gamma_{\text{TCMX}} \pm [(\gamma_{\text{TCMX}} \cdot CV_{\gamma_{\text{TCMX}}}) \cdot t(0.05; \nu)] \quad (5)$$

where $t(0.05; \nu)$ is the Student's t for a confidence level of 95% and ν degrees of freedom.

2.6.2. Extraction performance

2.6.2.1. Quality control procedure. The performance of the sample extraction is checked by the calculation of the ratio between H_{Ref} , from first S_{ref} analysis, and the signal of CHB from sample extract (molecular ion), H_{CHB} . The H_{CHB} is corrected to extract dilution performed by adding m_6 of S_{TCMX} to the fraction $m_5 - m_4$ of the original extract mass m_1 . The calculated γ_{CHB} (Eq. (6)), reported in arbitrary units, is not affected by sample dilution or GC–MS sensitivity variability.

$$\gamma_{\text{CHB}} = \frac{H_{\text{Ref}}}{[H_{\text{CHB}}/((m_5 - m_4)/m_3 \cdot V_E)]} \quad (6)$$

The γ_{CHB} value is affected twice by GC–MS repeatability (for H_{Ref} and H_{CHB}), by the reliability of estimated C_{Ref} , V_E , m_3 , m_4 , m_5 and addition of CHB to debris, and by the variability of transference of CHB from debris to sample extract. This transference depends on the efficiency of adsorption of CHB to ACS and of the extraction CHB from ACS to solution A. Both mass transfer steps are clearly the major sources of variability since CHB compete with sample components when are adsorbed by ACS. The γ_{CHB} is not expected to be equivalent to one since signals of different compounds (TCMX and CHB), function of their concentration and specific GC–MS sensitivity, are considered. A high efficiency of transference of CHB to sample extract produces larger H_{CHB} values and lower γ_{CHB} values than an estimated average.

2.6.2.2. Validation. The relative variability of γ_{CHB} values is expected to be higher than the observed for γ_{TCMX} values. This variability must be small enough to allow the detection of relevant deviation in CHB transference from debris to sample extract motivated by gross experimental errors or faults.

2.6.2.3. Quality control criterion. The routine control of sample extraction is performed by the calculation of a γ_{CHB} value for each

sample analysis and the evaluation of its positioning within the interval from Eq. (7). If this criterion is not fulfilled and no ILRs are detected, sample extraction must be repeated.

$$\gamma_{CHB} \pm [(\gamma_{CHB} \cdot CV_{\gamma_{CHB}}) \cdot t(0.05; \nu)] \quad (7)$$

2.6.3. Sample conservation

2.6.3.1. Quality control procedure. Similarly to the extraction performance evaluation, the fire debris sample conservation is checked by the calculation of the ratio between H_{Ref} , from first S_{Ref} analysis, and signal of DCB from sample extract (molecular ion), H_{DCB} . The H_{DCB} is corrected by extract dilution. The calculated γ_{DCB} (Eq. (8)) is not affected by sample dilution or GC-MS sensitivity variations.

$$\gamma_{DCB} = \frac{H_{Ref}}{[H_{DCB}/((m_5 - m_4)/m_3 \cdot V_E)]} \quad (8)$$

The γ_{DCB} is affected by the same factors affecting γ_{CHB} , where repeatability of DCB signals, instead of CHB signals, are to be considered, plus the stability of DCB from sampling to laboratory test. The γ_{DCB} is not expected to be equivalent to one due to the same reasons presented for γ_{CHB} . The relative variability of γ_{DCB} would be significantly larger than the observed for γ_{CHB} in case relative variability of DCB signals is significantly larger than variability of CHB signals and CHB concentration is significantly affected by the delay between sampling and laboratory test. In case, conservation stage is a major source of variability, smaller γ_{DCB} values are observed in well preserved samples.

2.6.3.2. Validation. A small relative variability of γ_{DCB} values suggest the adequacy of sample conservation procedure and allow the detection of deviations in routine sample conservation. The acceptable tolerance of γ_{DCB} values must be associated with detectable peaks of internal standard.

2.6.3.3. Quality control criterion. The sample conservation is checked by the calculation of a γ_{DCB} value for each sample and the evaluation of its positioning within the interval from Eq. (9). If this criterion is not fulfilled and no ILRs are detected, the test is considered inconclusive and, whenever possible, sample collection must be repeated.

$$\gamma_{DCB} \pm [(\gamma_{DCB} \cdot CV_{\gamma_{DCB}}) \cdot t(0.05; \nu)] \quad (9)$$

2.7. Quality control report

The developed quality control tools are particularly relevant to support negative results (e.g. when no residues of accelerants are identified). If quality control checks fail but accelerant residues are present, the bad performance of the procedure will not affect the reliability of the qualitative evaluation. On the other hand, a bad performance of the procedure turns negative results into inconclusive ones.

3. Results and discussion

3.1. Uncertainty associated with R

Table 2 presents the data used to calculate R of sample ACPU1. The input quantities values are presented with the respective standard uncertainty. The standard uncertainty associated with R , u_R , resulting from the combination of the uncertainty components using the numerical Kragten method [9,10], is reported at the bottom of the table. The relative standard uncertainty, u'_R ($u'_R = u_R/R$) associated with R is 1.54%. The CV_{R_H} is 7.42% ($CV_{Rep} = 5.25\%$) and 1/5 of this value (1.48%) is statistically equivalent to the u'_R proving its negligible magnitude considering the GC-MS repeatability intended to be controlled. Therefore, it can be concluded that the

Table 2

Evaluation of the uncertainty associated with R (C_{Ref}/C_{TCMX}): input and output quantities and respective standard uncertainties.

	Value	Standard uncertainty
Input quantities (variable)		
DCM mass for extraction mixture, m_{DCM} (g)	133.1700	0.0050
P mass for extraction mixture, m_P (g)	63.0110	0.0050
TCMX purity, Pur_{TCMX} (%)	97.50	0.72
Mass of TCMX for the preparation of the S_{TCMX} , m_{TCMX} (g)	0.0256	0.0035
Mass of TCMX + DCM for the preparation of the S_{TCMX} , m_{P3} (g)	66.3220	0.0035
Point 0: average mass of water in pycnometer, m_{pyc} (g)	24.50208	0.00050
Point 0: tabulated water volumic mass at $20 \pm 0.5^\circ\text{C}$, ρ_{20} (g/mL)	0.99820	0.00050
Point 1: DCM mass, $m_{DCM(1)}$ (g)	133.17100	0.00050
Point 1: P mass, $m_{P(1)}$ (g)	63.01100	0.00050
Point 1: average mass of mixture in pycnometer, $m_{pyc(1)}$ (g)	23.85912	0.00050
Point 2: DCM mass, $m_{DCM(2)}$ (g)	80.00500	0.00050
Point 2: P mass, $m_{P(2)}$ (g)	20.01000	0.00050
Point 2: average mass of mixture in pycnometer, $m_{pyc(2)}$ (g)	26.48987	0.00050
Point 3: DCM mass, $m_{DCM(3)}$ (g)	67.02600	0.00050
Point 3: P mass, $m_{P(3)}$ (g)	36.49000	0.00050
Point 3: average mass of mixture in pycnometer, $m_{pyc(3)}$ (g)	23.38077	0.00050
Average mass of the dispensed extraction mixture, m_3 (g)	0.961	0.017
Single mass of the empty vial with cap, m_4 (g)	2.7880	0.0035
Single mass of the vial, cap and transferred extract, m_5 (g)	3.5540	0.0035
Average mass of the dispensed S_{TCMX} , m_6 (g)	0.2509	0.0025
Average mass of the dispensed S_{TCMX} to prepare S_{Ref} , m_A (g)	0.2509	0.0025
Average mass of the dispensed S_A, m_B (g)	0.7735	0.0096
Output quantity		
$R = (C_{Ref}/C_{TCMX})^a$	0.991	0.015

^a Value from sample ACPU1.

developed procedure, both for the addition of TCMX in the sample extract and for the preparation of the external standard, is fit to the control of the GC-MS repeatability.

3.2. Variability of quality control parameters

Table 3 presents the height of the peaks of internal and external standards, observed from the analysis of samples (Section 2.2), and the respective γ_{DCB} , γ_{CHB} and γ_{TCMX} values.

It can be observed in **Table 3** that coefficient of variation of γ_{DCB} , γ_{CHB} and γ_{TCMX} values (37, 22 and 14%, respectively) are significantly smaller than coefficient of variation of the original H_{DCB} , H_{CHB} , H_{TCMX} and H_{Ref} values. Different H_{Ref} values are observed since tests were performed on different days and GC-MS sensitivity conditions.

It can be concluded, from these data, that γ_{DCB} , γ_{CHB} and γ_{TCMX} parameters are not affected by GC-MS sensitivity or sample dilution variations. More important, these parameters seem to be affected by a relative variability small enough to allow the detection of relevant deviations in test performance.

Table 3

Experimental parameters recorded from the analysis of samples from Table 1 and quality control parameters used to check performance of critical stages of the tests.

Sample	m_4	m_5	C_{TCMX}	H_{DCB}	H_{CHB}	H_{TCMX}	H_{Ref}	γ_{DCB}	γ_{CHB}	γ_{TCMX}
ACPU1	2.788	3.554	94.750	16,235	36,678	9962	10,242	0.517	0.229	1.037
ACPU2	2.811	3.631	89.681	70,387	87,379	27,178	26,264	0.310	0.249	0.923
ACPU3	2.828	3.628	91.494	29,909	63,942	18,792	19,632	0.542	0.253	1.018
ACPU4	2.348	3.096	96.569	11,607	22,166	7040	7699	0.541	0.283	1.125
ACPU5	2.321	3.094	94.061	23,503	68,849	21,980	24,205	0.845	0.288	1.103
ACPU6	2.327	3.170	87.682	31,068	121,389	41,100	39,598	1.063	0.272	0.900
ACPU7	2.265	3.044	93.478	37,944	181,648	47,655	35,289	0.764	0.160	0.737
ACPU8	2.291	3.059	94.552	22,955	72,794	16,989	19,335	0.690	0.218	1.146
ACPU9	2.357	3.121	95.049	59,999	59,943	30,857	28,125	0.384	0.384	0.922
ACPU10	2.250	3.032	93.190	13,296	25,427	9320	7287	0.451	0.236	0.776
ACPU11	2.816	3.587	94.257	25,522	99,041	28,664	27,681	0.889	0.229	0.969
ACPU12	2.306	3.127	89.592	71,255	96,557	33,079	38,015	0.443	0.327	1.096
CV (%)				62	57	52	47	37	22	14
Quality control criteria (conf. level 95%)								0.620 ± 0.427	0.261 ± 0.128	0.979 ± 0.303

4. Conclusion

It can be concluded by this work that the developed procedure to control GC–MS repeatability, sample extraction and sample conservation, in the detection of ILR in fire debris, based on ASTM E1412–07 and E1618–10 standards, is fit for its intended use. The proposed quality control procedure is easily implemented in routine since it just involves the addition of the internal standards, using an automatic pipette, and two weighing operations. The involved calculations can be easily performed in a simple spreadsheet program.

The developed internal standard technique can be used in any other analytical methods involving the concentration of the volatile fraction of sample in a solid phase from which analytes are extracted to a subsequently analysed solvent.

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